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(54) Biocides for treating industrial waters, particularly flue gas desulfurization scrubber sludge.

(57) Sulfate-reducing bacteria present in industrial waste waters can be controlled by using either the biocide glutaraldehyde or a blend of sodium dimethyldithiocarbamate and disodium ethylene bisdithiocarbamate.

EP 0 261 607 A2

This invention relates to a method of controlling sulfate-reducing bacteria present in industrial waste waters.

Certain industrial process waters become highly contaminated with sulfate-reducing bacteria, particularly the species, Desulfovibrio desulfricans. A good example of such industrial process water contamination is found in the sludges and slurries produced as a result of flue gas desulfurization (FGD) scrubbers. Such sludges or slurries are produced due to scrubbing gases in the stacks of large boilers such as are found in utilities. These large boilers utilize high sulfur fuels such as coal or high sulfur fuel and residual oils.

FGD system sludge contains high concentrates (>10%) of gypsum ($CaSO_4 \bullet 2H_2O$) and calcium sulfite hemihydrate ($CaSO_3 \bullet 1/2\ H_2O$). The lower areas of thickeners and ponds become anaerobic, resulting in an ideal growth environment for sulfate-reducing bacteria of the species Desulfovibrio. The growth of Desulfovibrio reduces sulfate and sulfite and evolves hydrogen sulfide (H_2S) gas to the atmosphere. Hydrogen sulfide generation is an odor problem even at low levels. The bacteria can also cause corrosion of construction materials. These problems are particularly severe in warm weather, such as in the summer season and much of the year in the southern United States. The use of biocides in actual FGD systems has been rather rare.

A common method of controlling sulfate-reducing bateria is the use of non-oxidizing biocides. These materials are well known and are illustrated by such well-known materials as methylene bis thiocyanate, metronidazole, and blends of certain dithiocarbamates and gluteraldehyde. 2,2′-dibromo-3-nitrilopropionamide (DBNPA) has shown some success in controlling sulfate-reducing bacteria in FGD systems.

It has been found, however, that when these industrial waters contain sulfate-reducing bacteria in quantities greater than 10 colonies per ml that sulfate-reducing bacteria controlling biocides are ineffective or require such large dosages as to be impractical.

Accordingly, the object of the present invention is to provide a method of controlling sulfate-reducing bacteria present in industrial waste waters.

The present invention provides a method of controlling sufate-reducing bacteria present in industrial waste waters which have a sulfate-reducing bacteria population greater than 10 colonies per ml which is characterized by treating such waters with an effective amount of a biocidal composition comprising either a blend of:

sodium dimethyldithiocarbamate and
disodium ethylene bisdithiocarbamate, or
glutaraldehyde.

The dosage of these biocides is usually within the range of between about 5-500 ppm per weight.

The invention will now be described in greater detail.

The literature is replete with references to biocides that are effective in controlling sulfate-reducing bacteria. Typical and illustrative, but non-inclusive of such materials, are the following biocidal solutions;

Composition No. 1 20% 2,2′-dibromo-3-nitrilopropionamide,

Composition No 2 1.15% 5-chloro-2-methyl-4-isothiazolin-3-one and 0.35% 2-methyl-4-isothiazolin-3-one

Composition No. 3 10% Methylene bis thiocyanate (MBT)

Composition No. 4 45% Glutaraldehyde

Composition No. 5 0.9% Metronidazole

Composition No. 6 a blend of 15% Sodium dimethyldithiocarbamate, and 15% Disodium ethylene bisdithiocarbamate

Composition No. 7 a solution of hexahydro-1,3,5-tris-(2-hydroxyethyl)-s-triazine.

Of the above biocides, preferred are Compositions Nos. 4 and 6 with Composition 6 being most preferred. These biocides may be used over a large dosage range depending upon the effectiveness of the biocides.

In addition to using the blend of carbamates described in Composition No. 6, other biocidally effective thiocarbamates may be used.

The invention is particularly effective in controlling flue gas scrubber sludges or slurries when th concentration of the sulfate-reducing bacteria is about or greater than 100 coloni s per ml.

The following is pr sent d by way of example:

Procedure

A quantity of thickener underflow sludge was obtained from three Southern utilities.

Tests were conducted on the fresh sludge within a week after the sample was taken except the sludge from Utility No. 1 which was about 1 month old. All of the biocides were incubated in the sludge using stoppered Erlenmeyer flasks at 30°C for 24 hr., initially at dosages of 200 and 2000 ppm. Triplicate 0 1 ml. inoculations were mixed into ferric citrate-sodium sulfite-tryptone agar medium (approximately 10-15 ml) for each of the sludge sample. Black iron sulfide colonies would develop in the agar due to growth of sulfate-reducing bacteria. The number of black Desulfovibrio colonies were counted after 48 hr., 72 hr., 96 hr. or 144 hr., depending on growth rate.

In the following testing of sludge from Utility No. 3, the sludge was:

1. First aerated with compressed air through a diffuser for one hour before the biocides were added to simulate forced oxidation;

2. Mixed with biocides in 100 ml open beakers at room temperature overnight using a stir plate and mixing bars before being cultured to simulate an open thickener; and,

3. Mixed with biocides at 10, 50 and 100 ppm concentration.

Results and Discussion

Thickener Underflow from Utility No. 1

The thickener underflow from Utility No. 1 was evaluated first to see if any of the biocides could succeed in killing Desulfovibrio in the high-sulfur containing FGD sludge. Five biocides, Composition Nos. 1, 2, 3, 5 and 6, were used at 200 ppm and 2000 ppm. The high dosage was utilized as the upper limit of a biocide program dosage.

A table summarizing results is given in Table I. The results of the blank without biocide treatment gave a low Desulfovibrio count of 5-10 ml of sludge. Of the five biocides, Composition No. 6 and Composition No. 5 gave effective kill at both 200 and 2000 ppm. The other biocides were ineffective at either dosages, except Composition No. 1 which was somewhat effective at 2000 ppm.

Thickener Underflow from Utility No. 2

The FGD sludge from Utility No. 2 was determined to contain 1000-1500 sulfate-reducing bacteria per ml. of sludge. This level of bacteria count is extraordinarily high for FGD sludge. Since this Utility uses waste water treatment plant effluent as makeup to their cooling towers, and the cooling system blowdown ends up as scrubber water makeup, high levels of bacteria in the FGD system could be expected. The sulfate-reducing bacteria in the system were at extremely high concentrations and are out of control in terms of population. Reports from the sales representative indicated the presence of strong hydrogen sulfide odors from the thickener (clarifier).

Three series of tests were conducted to determine the type and dosage of a biocide treatment program which can significantly reduce the population of Desulfovibrio.

In the first series of testing, dosages as high as 6000 ppm of non-oxidizing biocides such as Composition Nos. 1, 2, 3, 5 and 6 had little or no effect in reducing the Desulfovibrio population.

Table I

Bacterial growth versus biocide dosage for Utility No. 1

Composition No.	Dosage ppm	Culture Result Tube #1 72 hrs	144 hrs	Tube #2 72 hrs	144 hrs	Tube #3 72 hrs	144hrs
Blank	0	**1-2	* +	1-2	+	1-2	+
Blank	0	1-2	+	1-2	+	1-2	+
6	200	0	1	0	1	0	1
6	2000	0	0	0	0	0	0
1	200	0	+	1-2	+	0	+
1	2000	0	0	0	+	0	0
5	200	0	0	0	0	0	0
5	2000	0	0	0	0	0	0
2	200	1-2	+	0	+	1-2	+
2	2000	0	0	1-2	+	0	+
3	200	0	+	0	0	0	+
3	2000	0	0	1-2	+	0	0

NOTE: * -"+" means complete bacterial growth (black tube)
** - Approximate number of colonies counted.

Thickener Underflow from Utility No. 3

Utility No. 3 was using Composition 1 to treat its FGD system thickener sludge for Desulfovibrio. The product was added once a week at 10 ppm dosage to the top of the thickeners and was found effective. Lower counts were obtained after biocide addition. The sludge tumed from a dark to a light color immediately after the application according to the operators.

Laboratory Testing at Lower-Oxygen Condition -

The sludge after Composition 1 treatment for one week showed a medium level of 100-200 bacteria per ml. of sludge. It was concluded that Composition No. 6 and Composition No. 4 showed the best killing at both 200 ppm and 2000 ppm. Composition No. 1, the biocide in use at the Plant, as well as Composition No. 2, No. 3 and No. 5 was not effective at 200 ppm dosage.

Laboratory T sting at More Aerated Condition -

Under the more aerated condition t sting, similar conclusions to the arli r findings were drawn: Composition No. 6 and Composition No. 4 again surfaced as the best biocides among all tested including a newly added Composition No. 7. These two biocides outperformed th DBNPA.

An evaluation comparing various biocides using an aerated type test method with constant mixing in an open atmosphere showed little or no difference to those using closed Erlenmeyer flasks. However, a low r dosage was needed under the aerated or oxygenated condition.

Due to aging of the sludge during transportation to the laboratory, resulting in increased numbers of sulfate-r ducing bacteria, exact dosage of biocide treatment for the actual FGD syst m should be determine on-site using the same procedure. This part of the result indicates that trends of biocide performance can be evaluated for any sludge in the lab.

The results are listed in Tables II and III. The data represents the number of colonies seen growing in the culture test tubes.

The results from Table II indicate that the bacteria in the sludge overgrew the tubes because the populations were still too high. Composition No. 4 at 50 ppm and 100 ppm effectively kills the bacteria. Composition No. 6 showed the second best results. The test was repeated (Table III) but more oxidation of the sludge was allowed before biocides were added, and stirred overnight. This time Composition No. 6 clearly reduced the bacteria population at 50 ppm and 100 ppm dosages. With more oxidation in the sludge, dosage requirement should be even lower. Under these more oxygenated conditions, Composition No. 6 was the choice over Composition No. 4.

Table II

Biocide Test Results
48 Hours Incubation, Utility No. 3 Sludge

Composition No.	Dosage ppm	Tube Results 1	2	3
Blank	0	B*	B	B
6	10	B	B	B
4	10	1/2 B	1/2 B	1/2 B
7	10	1/2 B	B	B
2	10	B	B	1/2 B
6	50	B	1/2 B	30
4	50	** 10	10	10
7	50	B	B	1/2 B
2	50	B	1/2 B	B
6	100	B	50+	50+
4	100	50+	50+	30+
7	100	B	B	B
2	100	B	B	B

* B - tube is black with growth
** Number represents the number of colonies

Table III
Biocide Test Results - Utility No. 3

Composition No.	Dosage ppm	Tube Results 1	2	3
Blank	0	100	30	30
1	10	20	20	20
6	10	20	30	50
4	10	30	30	30
1	50	10	10	10
6	50	0	5	5
4	50	20	20	0
1	100	50	50	10
6	100	0	0	0
4	100	20	20	20

Claims

1. A method of controlling sulfate-r ducing bacteria pr sent in industrial waste waters which have a sulfate-reducing bacteria population greater than 10 colonies per ml which is characterized by treating such waters with an ffective amount of a biocidal composition comprising either a blend of:

sodium dimethyldithiocarbamate and
disodium thylene bisdithiocarbamate, or
glutaraldehyd .

2. The method of claim 1, characterized in that the biocide is a blend of sodium dimethyldithiocarbamate and disodium ethylene bisdithiocarbamate.

3. The method of claim 2, characterized in that the biocide is glutaraldehyde.

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EP 0 261 607 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 11 3703

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-4 495 200 (LINDSTROM et al.) * Claim 1; column 3, example 1, table 1 * --	1,2	C 02 F 1/50
X	US-A-2 801 216 (YODER et al.) * Whole document * --	1,3	
X	CHEMICAL ABSTRACTS, vol. 92, no. 26, June 30, 1980, page 130, ref. no. 217683j; Columbus, Ohio, US; T.A. KUZNETSOVA et al.: "Effect of bactericides on sulfate-reducing bacteria" & NEFTEPROMYSL. DELO 1980, (1), 32-4 * Abstract * --	1,3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
Y	GB-A-2 118 925 (DEARBORN' CHEMICALS) * Abstract; page 2, lines 10-34, example C * --	1,3	C 02 F
Y	LEHR- UND HANDBUCH DER ABWASSER-TECHNIK, 3rd Ed., vol. VI: "Organisch verschmutzte Abwässer sonstiger Industriegruppen", February 1986; Ernst & Sohn, Berlin, DE * Page 339, last 3 lines * --	1,3	
A	US-A-3 973 034 (BUCKMAN) * Column 8, line 25 - column 9, line 4 * -- ./.	1,2	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02-02-1989	KASPERS

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if c mbined with an ther document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for ther reasons

& : m mber of the same patent family, corresponding d cument

European Patent Office

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid.

namely claims:

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

X LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,

namely:

1. Claims 2 and 1 as far as the blend of sodium-methyldithiocarbamate and disodiummethylene bisdithiocarbamate is concerned

2. Claims 3 and 1 as far as glutaraldehyde is concerned

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid,

namely claims:

☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,

namely claims:

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 87 11 3703

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 129 315 (ECONOMICS LAB.) * Claim 3 *	1,2	
O	COLLOQIUM INT. BACTERIOLOGY, March 2, 1984. & CHEMICAL ABSTRACTS, vol. 108, no. 1, January 4, 1988, page 160, ref. no. 1641v; Columbus, Ohio, US; & IFREMER 1986, 3, 617-19 * Abstract *	1,3	
A	CHEMICAL ABSTRACTS, vol. 102, no. 11, March 18, 1985, page 289, ref. no. 92444y; Columbus, Ohio, US; C.C. GAYLARDE et al.: "Some recommendations for sulfate-reducing bacteria biocide tests" & J. OIL COLOUR CHEM. ASSOC. 1984, 67(12), 305-9 * Abstract *	1,3	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	GB-A-2 138 799 (DEARBORN CHEMICALS) * Page 2, lines 8,12-15 *	1-3	
A	US-A-3 892 588 (HORNE)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alon
Y : particularly relevant if combined with another d cument f the same categ ry
A : technological background
O : non-written disclosure
P : intermediate document

T : the ry r principle underlying the inventi n
E : earlier patent document, but published n, or after the filing date
D : document cited in the applicati n
L : document cited f r other reasons
& : member of the same patent family, corresponding document